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Selective Complexation Leaching of Cobalt Using Histidine in Alkaline Medium

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Abstract: For the extraction of cobalt from cobalt-rich alloy slag, ammonia was considered a lixiviant with limited environmental impact compared to acid lixiviant. However, problems such as large ammonia volatilization loss, toxic vapor emissions, and suboptimal process control were encountered during ammonia leaching. To address these issues, a new method was proposed for recovering cobalt via selective complexing leaching, where an alkaline histidine solution was utilized instead of ammonia. A high cobalt leaching rate of 99% was achieved under the following conditions: a leaching temperature of 35℃, a histidine/cobalt molar ratio of 1.5, a pH range of 6–11, a leaching duration of 6 hours, and a stirring speed of 300 rpm. In the verification test for the leaching of Cu-Co alloy slag with histidine, cobalt was almost entirely leached, while iron, lead, and copper were observed to be difficult to leach. The kinetic analysis of the cobalt leaching process revealed that electrons were donated to Co^{2+} by the amino and COO^- groups in histidine during the coordination reaction. This confirmed that a soluble complex, $Co(C_6H_9N_3O_2)_2$, was formed through coordination between histidine and Co^{2+}.

Keywords: cobalt; leaching; histidine; cobalt-rich alloy slag

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1. Introduction

The lower grade of cobalt ores and the increased demand for cobalt have stimulated the development of methods for recovering Co from low-grade metallurgical waste resources. Cu-Co alloy slag is obtained from converter slag which is reduced by electric furnace and water quenched. The grade of cobalt in the alloy slag is much higher than that in the ore. Currently, the main methods for processing Co ore include hydrometallurgical and pyrometallurgical approaches[1-4]. Compared to pyrometallurgical processes, hydrometallurgical processes have demonstrated higher metal recovery efficiency, achieving both high product purity and substantial energy savings[5]. At present, the hydrometallurgical methods for extracting Co from cobalt ores involve acid leaching[6], alkaline leaching[7], and bioleaching[8]. In acid leaching processes, HCl, H2SO4, HNO3 and other strong acid solutions are used as leaching agents, harmful gases such as Cl2, SO3, or NOx are released. The residual acids after leaching have a significant impact on the environment, which cannot be ignored.[9].The ammonia leaching process has always been an effective method for extracting metals from minerals[10]. However, from an operational perspective, the volatile characteristics of ammonia will lead to environmental and health risks. High concentrations of ammonia have been maintained throughout the leaching process, resulting in significant ammonia losses. Additionally, ammonia is explosive under high temperature and pressure[11]. Amino acids (such as glycine) have been proven to be environmentally friendly and effective reagents, capable of selectively leaching various metals from a range of minerals under alkaline conditions [12]. Therefore, replacing ammonia with amino acids as leaching agents for metal recovery may be a better choice.

A. Oraby et al.[13] were the first to propose the leaching of Cu and Au with glycine. Chen et al.[14] used glycine to leach Co and Li from spent lithium-ion batteries. The highest extractions of 97.07% for Co and 90.95% for Li were achieved at glycine concentration of 300 g/L, 10% H2O2, solid-to-liquid molar ratio of 1:100, temperature of 80℃, and leaching time of 7 h. Manivanna et al.[15] achieved the cobalt leaching recovery of 89.7% from Li+ batteries (LiBs) using glycine at 100 ℃, slurry concentration of 13.8 g/L, and glycine concentration of 1.24 M. E.A. Oraby et al.[16] employed an alkaline glycine leaching system to selectively extract Ni and Co successively from serpentine-rich low-grade sulfide ores. It was shown that Ni and Co could be selectively leached using glycine, but the leaching rate was very slow, with 83.5% and 76.3% of nickel and cobalt being leached in 672 h. The effectiveness of glycine-based metal recovery solutions was further validated through multiple technologies, including solvent extraction, sulfide precipitation, carbon adsorption, ion exchange, and chemical reduction[17]. Recyclability of glycine was confirmed by Eksteen and Tanda[18], particularly in multi-stage extraction systems and reused lean solutions. Despite these advancements, challenges such as prolonged leaching rates and high amino acid costs were identified, underscoring the need for developing novel amino acid leaching systems to enhance both universality and economic viability.

Histidine was also a naturally basic amino acid, which contained an amino group (NH2), a carboxyl group (-COOH) and an imidazole ring (1H-imidazole). Various molecular forms were exhibited by it at different pH values[19]. The isoelectric point (pI) of histidine was 7.59. It was polar, easily dissociable and hydrophilic, and was the only amino acid that was buffered at near neutral pH[20]. Metal-amino acid complexes with cyclic structures were formed by the amino and carboxyl groups of amino acids and metal ions in a certain ratio[21]. Currently, histidine had been successfully applied as a ligand in the synthesis of many metal nanoparticles, such as gold[22], silver[23], copper[24], etc. The leaching of gold was promoted by J.J. Eksteen et al.with an amino acid mixture (glycine and histidine) under conditions of 0.1 M amino acid, 1% H2O2, pH 11, and 60℃.In this study, pure metal cobalt powder was first intended to be used as the research object to investigate the reaction mechanism of cobalt leaching with histidine. After systematically studying the influence of key leaching parameters such as leaching temperature, reagent concentration, stirring speed, histidine/Co molar ratio and pH, a series of characterization techniques, such as FT-IR, SEM-EDS and XPS, were adopted. The leaching kinetics model of histidine on pure metal cobalt powder was established to further analyze the leaching mechanism of cobalt with histidine. Finally, Cu-Co alloy slag was used to verify the selective leaching effect of histidine on cobalt.

2. Materials and Methods

2.1 Materials

The chemical reagents used in the experiment include lysine (C6H14N2O2), histidine (C6H9N3O2), glycine (C2H5NO2), arginine (C6H14N4O2), citrulline (C6H13N3O3), theanine (C7H14N2O3), sulfuric acid (H2SO4), sodium hydroxide (NaOH) were analytically pure reagents, purchased from Sinopharm Chemical Reagent Co, Ltd. (Shanghai, China). The cobalt used in the experiment is 99.99% cobalt powder with the particle size of 90% -200 mesh. The Cu-Co alloy slag sample was obtained from the converter slag during the copper smelting process through reduction smelting and water quenching. Detailed chemical compositions of the alloy are shown in Table 1. All analytical samples were prepared with deionized water.

Table 1. Chemical compositions of the Cu-Co alloy slag

Elements	Co	Cu	Fe	Pb	Ni
Wt.%	6.2	30.7	61.2	1.4	0.42

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2.2. Leaching experiment

1 g of cobalt powder was used for leaching and various amino acids were used as leaching agents. Amino acid solutions were added at different concentrations and the molar ratio of amino acid to cobalt. The pH was adjusted to between 7-12 using 1% NaOH solution. The mixtures were then stirred continuously for 1 to 6 hours at different temperature with varying stirring speed. Samples were extracted periodically to determine the cobalt concentration. After the leaching process was completed, the residue was filtered, then dried at 105℃ for 3 hours, and weighed. The concentration of cobalt ions in the filtrate was analyzed using a flame atomic absorption spectrometer.

10 g of Cu-Co alloy slag sample was used for leaching at an initial pH of 8, a temperature of 35°C, a histidine concentration of 0.1 M, and a histidine/Co molar ratio of 1.5:1.The mixtures were then stirred continuously for 6 to 24 hours. Samples were extracted periodically to determine the ion concentrations of Co,Cu,Pb,Fe. After the leaching process was completed, the residue was filtered, then dried at 105℃ for 3 hours. The residual metals content in the filter slag were analyzed. The leaching rates of Co,Cu,Pb,Fe were calculated.

2.3. Analytical method

The chemical environment and valence state alterations of elements throughout the leaching process were examined using X-ray photoelectron spectroscopy(XPS K-Alpha, USA). The surface morphology of the leaching residue was scrutinized with a scanning electron microscope (SEM Regulus8100, brand, Japan), while the functional group bonding changes of the amino acids before and after the leaching reaction were analyzed using Fourier transform infrared spectroscopy(FT-IR NEXUS 670, Nicolet, USA). The concentration of metal ions was quantified employing a flame atomic absorption spectrometer (AAS, 55B AA, Agilent Technologies Inc), and the leaching rate of cobalt was computed as per formula (1).

$$\mathrm{X_{Me}} = \frac{\mathrm{C_{Me}} \times \mathrm{V}}{\mathrm{m} \times \omega_{\mathrm{Me}}} \times 100\% \qquad （1）$$

Where X_{Me} is the leaching rate of cobalt, %; C_{Me} is the concentration of cobalt determined by flame atomic absorption spectrometry, mg/L; V is the volume of the filtered leaching solution, L; m is the mass of cobalt powder, mg; ω_{Me} is the mass fraction of cobalt (purity), %.

3. Results

3.1. Comparison of the leaching effects of different types of amino acids on cobalt Subsection

The effects of four different amino acids with varying numbers and positions of amino groups on cobalt leaching were studied, including glycine (Gly), histidine (His), lysine (Lys), citrulline (Cit).

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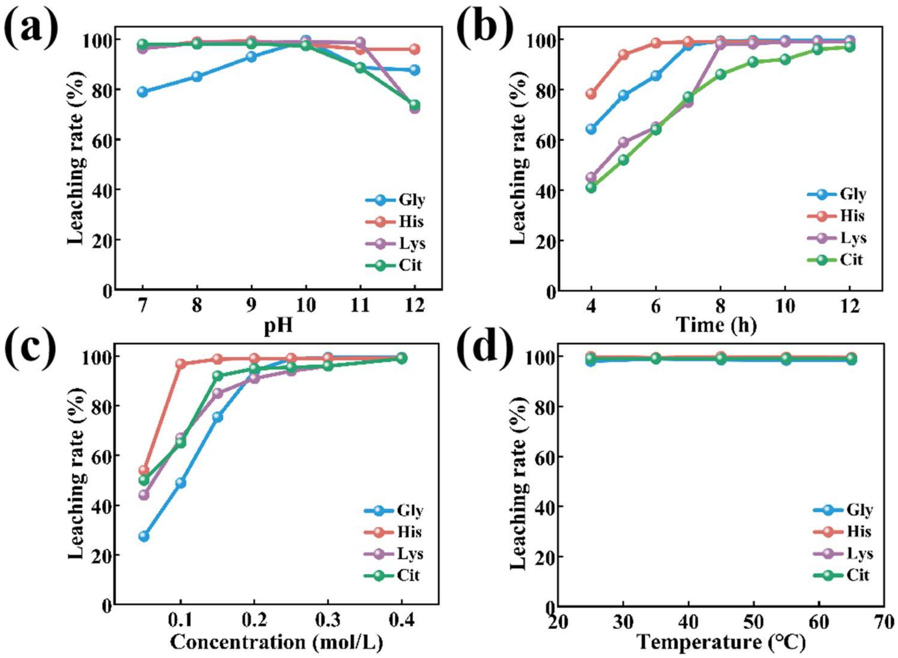

Figure 1. The leaching effects of different amino acids on cobalt varying with different pH (a), leaching time (b), amino acid concentration (c), and leaching temperature (d).

The structure of amino acids is influenced by pH, because their charge distribution and intermolecular interactions vary at different pH conditions. The results in Fig.1a (leaching condition: amino acid concentration of 0.3 M, 5 mL 30% H_2O_2, 8 h, room temperature) demonstrate that histidine, lysine, and arginine all show good leaching effects on cobalt in the pH range of 7 to 10, while the leaching efficiency of cobalt from glycine increased with increasing pH. At pH 11, the leaching rates of histidine and lysine exceed 95%, while the leaching efficiencies of arginine and glycine decrease to below 90%. At pH 12, the leaching efficiencies of the four amino acids on cobalt significantly declined. As a result, in subsequent experiments, the pH for glycine was set at 10, whereas the pH for the remaining three amino acids was set at 8.

The effect of leaching time on cobalt extraction efficiency of the above amino acids under suitable pH conditions is shown in Fig.1b. The experimental results indicated that the cobalt leaching rates of the four amino acids were different, among which histidine leached cobalt the fastest, and all the cobalt was leached within 6 hours. The order of the leaching rate was histidine, glycine, lysine and citrulline. Therefore, the leaching times of histidine, glycine, lysine and citrulline were set at 6, 7, 8 and 12 h, respectively, in the subsequent experiments.

Fig.1c shows that the rate of cobalt increases with the increase in amino acid concentration. When the concentration of histidine was 0.1 mol/L, cobalt was completely leached. However, for other amino acids, the leaching rate of cobalt exceeds 90% only when their concentration was above 0.25 mol/L. Therefore, in subsequent experiments, the concentration of histidine was set at 0.1 mol/L, while the concentration of other amino acids was set at 0.25 mol/L.

The results in Fig.1d indicated that temperature has a minimal effect on the leaching of cobalt by amino acids relative to other leaching parameters. In summary, under the conditions of 0.1 mol/L histidine concentration, histidine/Co molar ratio of 1.8:1, room temperature, pH 8, and leaching for 6 hours, cobalt was completely leached. Thus, histidine is the best choice of amino acid for subsequent experiments.

3.2 Parameter optimization

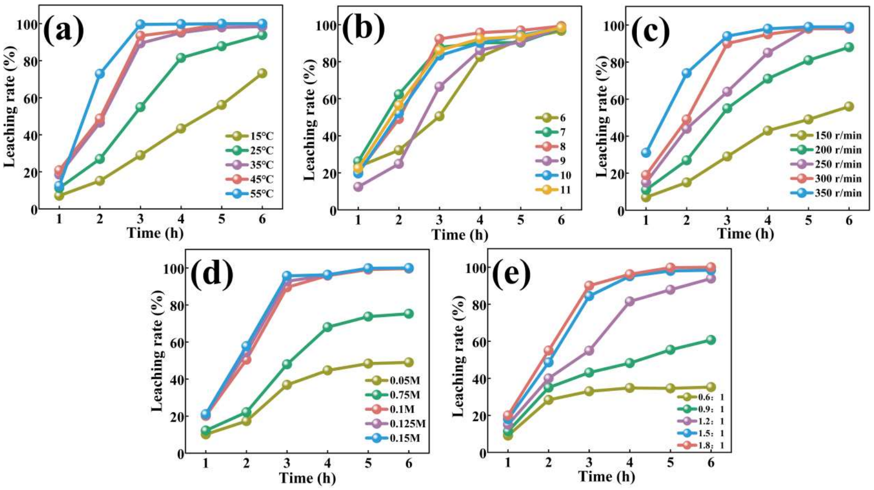

Figure 2. The effects of different factors on the extraction of cobalt using histidine: (a) temperature; (b) pH; (c) rotation speed; (d) histidine concentration; (e) molar ratio.

3.2.1 Effect of temperature

The effect of leaching temperature on the extraction of cobalt using histidine is shown in Fig.2a. Leaching temperature has a significant impact on the leaching efficiency of cobalt. The higher the temperature, the faster the leaching rate. Under the conditions of 0.1 mol/L histidine concentration, histidine/Co molar ratio of 1.8:1, pH 8, the complete leaching of cobalt was achieved in 3 h at 55°C. At 45°C and 35°C, complete leaching was achieved in 5 h. At room temperature, complete leaching was achieved in 6 h. This phenomenon is attributed to the increase in the rate constant K of leaching reaction kinetics at higher temperatures, which accelerates the Brownian motion in cobalt powder, improves the diffusion and mass transfer efficiency within the leaching system, thus, promotes the leaching efficiency of cobalt. 35°C was chosen for the subsequent experiments, where the leaching rate of cobalt reached 99% at 6h.

3.2.2 Effect of pH

To investigate the leaching efficiency of cobalt using histidine at different pH values, the leaching kinetics of cobalt were examined under controlled conditions: histidine concentration of 0.1 mol/L, histidine/Co molar ratio of 1.8:1, temperature of 35℃, and stirring speed of 300 rpm. As shown in Fig.2b, when the pH value is 8, the leaching rate of cobalt using histidine reaches up to 95% after 4 hours. In general, as long as the leaching time is sufficient (extended to 6 hours), cobalt can be completely leached under various pHs (pH 6-11). This phenomenon can be attributed to the buffering capacity of the histidine solution leaching system, which consists weak bases and acids, maintaining pH stability within a certain range, and thus ensuring a sustained high cobalt extraction rate.

3.2.3 Effect of stirring speed

The increase in stirring rate promotes the diffusion of oxygen and histidine in the leaching system, enhancing mass transfer between the liquid phases and cobalt powder, which in turn accelerates the leaching rate of cobalt. As shown in Fig.2c, the leaching rate of cobalt is positively correlated with stirring rates from 150 to 350 rpm. This phenomenon indicated that the stirring rate not only enhances the relative motion between the solid phase and the liquid phase (helping the leaving out of leach product, i.e., complexed cobalt ions) during the leaching process but also increases the concentration gradient of reactants in the liquid film, thereby accelerating diffusion and improving leaching efficiency. After considering both leaching efficiency and energy consumption, the stirring speed of 300 rpm was determined, at which the cobalt leaching rate reached 99%.

3.2.4 Effect of histidine concentration

Fig.2d indicated the effect of histidine concentration on cobalt leaching rate. As the concentration of histidine increases, the leaching rate of cobalt also increases. When the histidine concentration was 0.05 mol/L, the leaching rate of cobalt after 6 h was only 53%. However, when the histidine concentration was 0.1 mol/L, the leaching rate of cobalt after 4 h reached 95%. When the histidine concentration exceeds 0.1 mol/L, the leaching rate after 4 h was over 95%. The leaching rate of cobalt after 6 h reached 99%. The phenomenon demonstrated that high concentrations of histidine provide sufficient histidine ligands to coordinate with cobalt, thereby increasing the leaching rate.

3.2.5 Effect of His/Co molar ratio

The molar ratio of histidine to cobalt is crucial for improving the leaching efficiency of cobalt. The results in Fig.2e indicated that the leaching rate of cobalt increases with the amount of histidine. When the molar ratio was 1.5:1, the leaching rate of cobalt reached over 95%. However, further increasing the amount of histidine does not significantly improve the leaching rate of cobalt. Therefore, an excessively high molar ratio will instead increase the consumption of histidine. Thus, the molar ratio of histidine to cobalt was set at 1.5:1.

3.2.6 Selective leaching of Cu-Co alloy slag

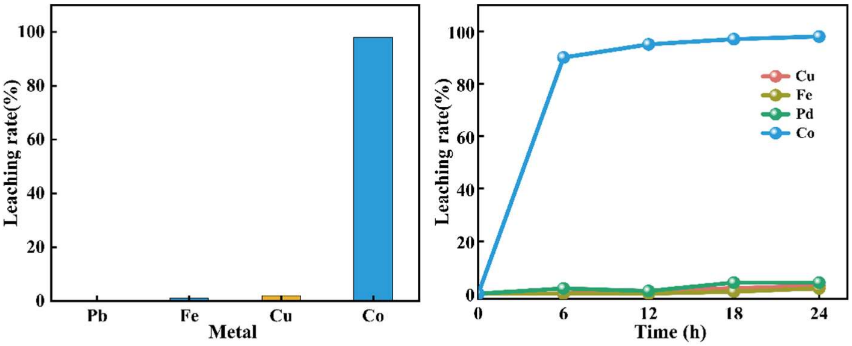

Figure 3. Selective leaching of Co from Cu-Co alloy slag under optimized conditions .

To determine the selective leaching effect of histidine on Cu-Co alloy slag, the leaching rates of Cu, Fe, Co, Pb in a copper-cobalt alloy slag were shown in Fig.3(a) The results indicated that the leaching rate of Co(88%) by histidine is significantly higher than that of Fe, Pb, and Cu, and copper.The effect of leaching time on histidine leaching of alloy slag are shown in Figure 3(b). When the leaching time was 12 hours, the leaching rate of Co was reached 95%, while the leaching rates of Fe, Pb, and Cu were 0.7%, 1%, and 1%, respectively. When the leaching time was extended to 24 hours, the leaching rate of Co was further increased to 98%, while the leaching rates of other metals remain almost unchanged. The results demonstrated that histidine leaching process has excellent selective extraction effect on cobalt from alloy slag.

4. Discussion

4.1 characterization analysis

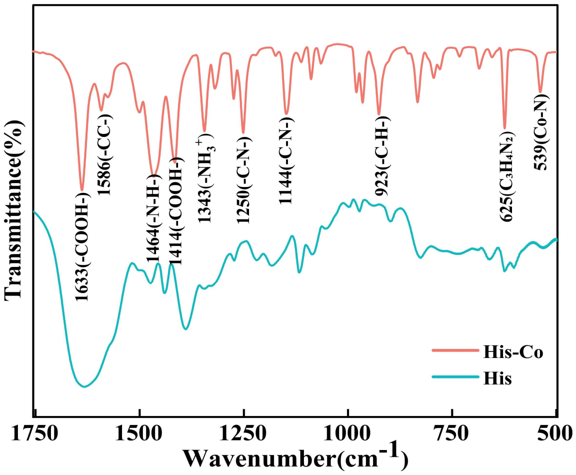

Figure 4. FT-IR of histidine and the solid product from the leaching solution treated by freeze-drying.

The FT-IR spectra of the solid product from the leaching solution treated by freeze-drying (His-Co) and L-histidine were shown in Fig.4. The infrared spectrum of histidine-cobalt sample showed significant differences compared to that of histidine. The positions of the main absorption peaks were obviously shifted, and the intensity of the peaks changed, indicating a chemical reaction between histidine and cobalt. Compared with histidine, the N-H stretching vibration peak in His-Co was red-shifted, i.e., the frequency decreasing from 1475 cm^{-1} to 1464 cm^{-1}, indicating the weakening of the N-H bond strength and the complexation reaction between the amino group and Co^{2+} ions. The symmetric stretching vibration peak of COO- shifted from 1437 cm^{-1} to 1414 cm^{-1}, which is due to the complexing of COO- with Co^{2+} ions, resulting in a decrease in the electron cloud density of the COO- group. The COOH absorption peak at 1633 cm^{-1} narrows significantly, which is attributed to the weakening of intermolecular or intramolecular interactions, resulting in an increase in the freedom degree of molecular, and the vibration frequency is concentrated as a narrowing of the peak[26]. However, the peak at 1586 cm^{-1} corresponds to the asymmetric CC bond stretching vibration of the imidazole ring[27], which is not present in the infrared spectrum of L-histidine. Furthermore, new characteristic peaks appeared in the spectrum of His-Co at 1343 cm^{-1}, 1250 cm^{-1} and 923 cm^{-1}, which corresponded to the asymmetric stretching absorption peaks of NH^{3+}, C-N, C-N/N-H and C-H, respectively[28-30]. The asymmetric stretching vibration peak of C-N shifted from 1114 cm^{-1} to 1084 cm^{-1} further confirming the involvement of the amino group in the reaction[31]. It is noteworthy that the strong absorption peak at 625 cm^{-1} originates from the vibration of the imidazole ring. The Co-N vibration peak at 539 cm^{-1} directly reveals the coordination relationship between the amino group and the cobalt ion. Based on FT-IR analysis, it was speculated that the amino group and COO- group in histidine played a complexing role in the cobalt leaching reaction.

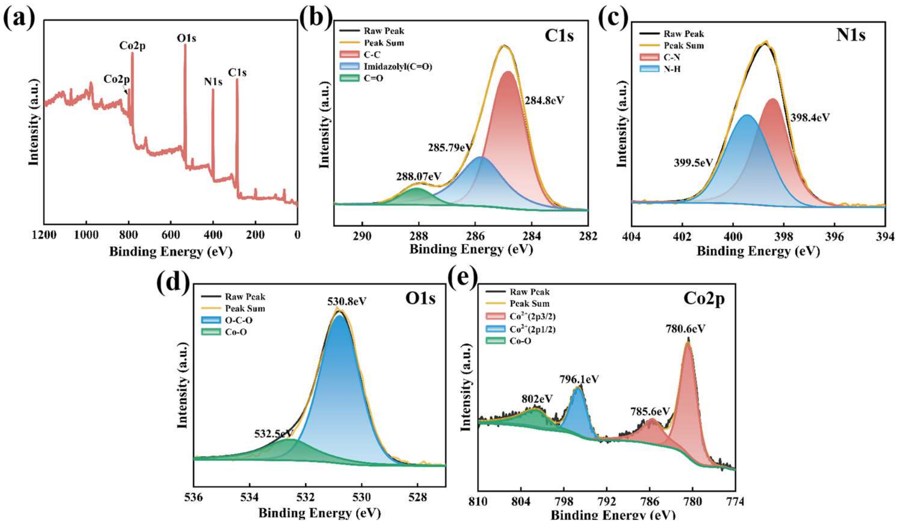

Figure 5. XPS spectra of the solid product from the leaching solution treated by freeze-drying.

Fig.5a presents the comprehensive XPS spectrum of the main elements in the leaching solution. After comparing the peak binding energies of the elements in leaching solution to those of standard spectra, the analysis results are shown in Fig.5b-e. Fig.5b illustrates the C1s spectrum with three peaks at 284.8 eV, 285.79 eV, and 288.07 eV, corresponding to the orbital binding energies of C1s in sp_2 or sp_3 hybridized C-H or C-C bonds, the C=N in the imidazole group of histidine, and the C=O bond[32]. In Fig.5c, N1s peaks at 398.4 eV and 399.5 eV are attributed to C=N and $CO\text{-}NH_2$, respectively. Fig.5d shows that the O1s peaks of the main oxygen-containing groups are located at 530.8 eV and 532.5 eV, which belong to the bands of O-C-O and CoO[33], respectively. The content of O-C-O is dominant, indicating that there was still unreacted histidine in the leaching solution. The peaks of 802 eV and 796.1 eV in Fig.5e correspond to the Co $2p_{1/2}$ orbital characteristic peaks of CoO and Co^{2+}, respectively, while the peaks of 785.6 eV and 780.6 eV represent the Co $2p_{3/2}$ orbital characteristic peaks of CoO and Co^{2+}[34]. The coexistence of O1s and Co2p peaks for CoO indicated the bonding of O atoms with Co ions. Based on these analyses, it was concluded that metallic Co was leached as Co^{2+}during the process. Considering the orbital binding energies of Co and C/O/N atoms in functional groups, it was inferred that electrons were donated to Co^{2+} by the amino and carboxyl groups of histidine during coordination. This finding was consistent with the XPS peak of Co^{2+} (796.1 eV), which matched reported values for Co-histidine complexes, confirming the formation of $[Co(His)_2]^{2+}$. Additionally, the FT-IR results (N-H shift from 1475 to 1464 cm^{-1}) further supported the proposed coordination mechanism via amino and carboxyl groups.

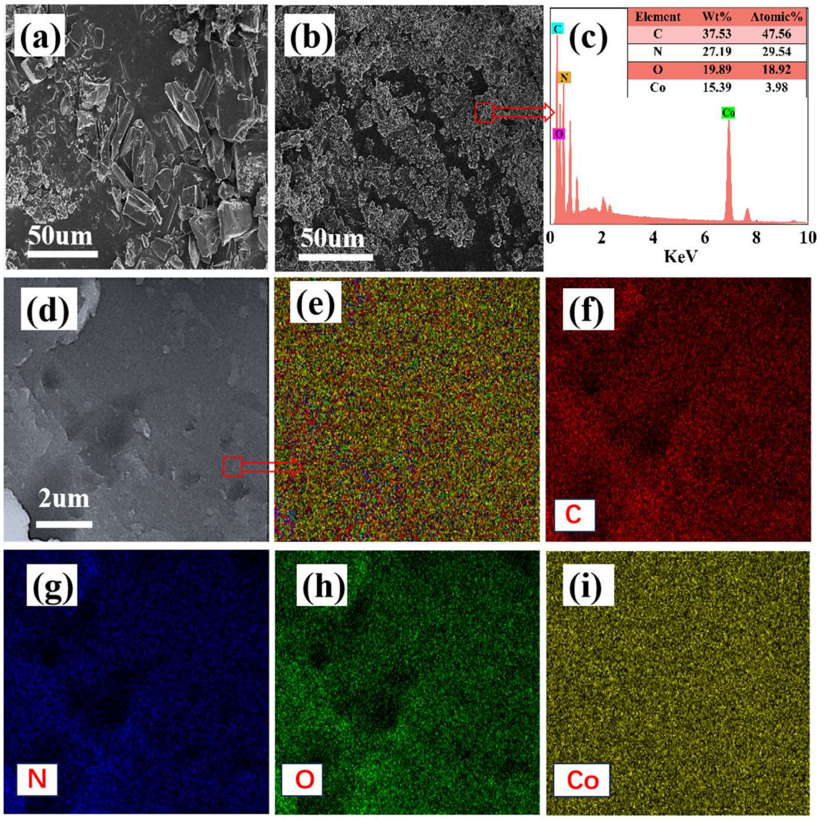

Figure 6. SEM-EDS analyses of cobalt powder(a) and the solid product from the leaching solution treated by freeze-drying(b-i).

As shown in Fig.6 (a-b), the SEM analyses revealed the surface morphology characteristics of the original cobalt powder and the solid product from the leaching solution treated by freeze-drying. Compared with the irregular strip morphology of the original cobalt powder, the cobalt surface after reaction with histidine exhibits the phenomenon of leaching corrosion. Fig.6c showed the EDS analysis of the solid product from the leaching solution treated by freeze-drying, and the content ratios of elements such as C, H, O, and Co were very close to those of $Co(C_6H_9N_3O_2)_2$. Combined with the previous FT-IR and XPS analyses, it was verified that O-C-O and -NH- in histidine formed metal ligands with cobalt ions. The mechanism of cobalt leaching by using histidine could be described as shown in Fig.7.

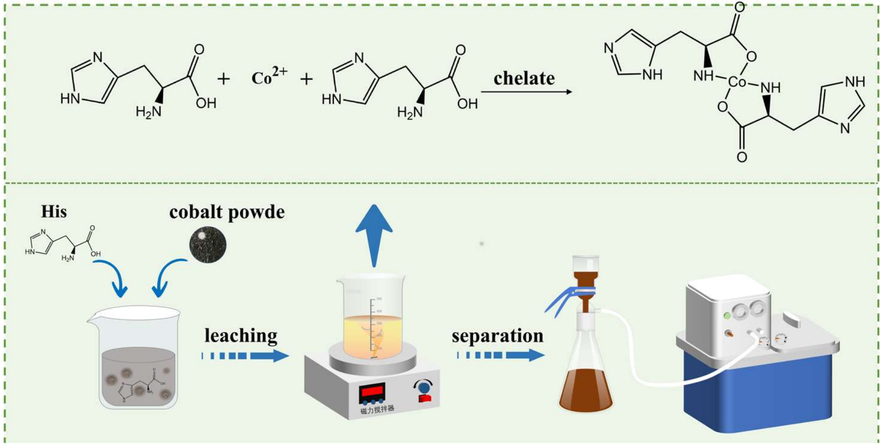

Figure 7. The mechanism of cobalt leaching by using histidine.

4.2 Leaching kinetics

To describe the reaction kinetics mechanism of cobalt leaching by histidine, the film diffusion model (Eq.2), chemical reaction control model (Eq.3) and product layer diffusion control model (Eq.4) and mixing control model (Eq.5) are used and fitted to identify the leaching process rate-controlling step [35,36].

$$X = kt \qquad (2)$$

$$1-(1-X)^{\frac{1}{3}} = kt \qquad (3)$$

$$1-\frac{2}{3}X-(1-X)^{\frac{2}{3}} = kt \qquad (4)$$

$$\frac{1}{3}\ln(1-X)+(1-X)^{\frac{-1}{3}}-1 = kt \qquad (5)$$

Where x is the leaching rate of metal, t is the leaching time (h), and k is the constant of apparent rate.

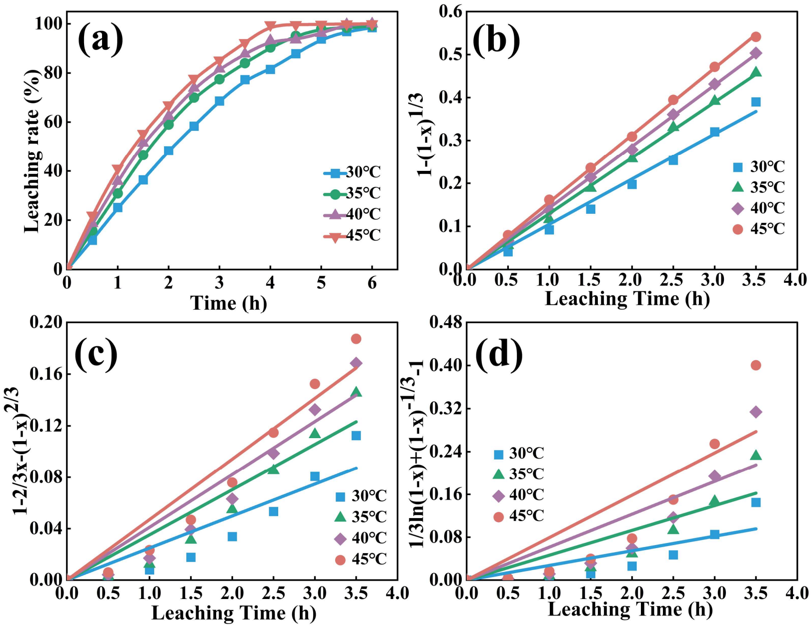

Figure 8. Equations fitting of the chemical reaction equation model (b), the internal diffusion equation model (c), and the mixed control model (d).

Table 2 The equations fitting parameters of the three kinetic models for cobalt leaching using histidine

Temperature (℃)	Internal diffusion control 1-(2/3)x-$(1-x)^{2/3}$		Chemical reaction control 1-$(1-x)^{1/3}$		Mixed control 1/3ln(1-x)+$(1-x)^{-1/3}$-1	
	k_1(min^{-1})	R_2	k_2(min^{-1})	R_2	k_2(min^{-1})	R_2
30	0.02493	0.846	0.05406	0.989	0.02732	0.716
35	0.03519	0.902	0.08991	0.998	0.04637	0.765
40	0.04110	0.911	0.13334	0.999	0.06148	0.747
45	0.04709	0.929	0.17980	0.999	0.07924	0.752

As illustrated in Fig.8 and Table 2, the fitting coefficient (R_2) of the equation of the surface chemical reaction control model exceeds 0.98 at different temperatures, indicating that the surface chemical reaction control model has a good linear relationship with the cobalt powder leaching time, and is significantly higher than the correlation coefficient obtained by the fitting of the internal diffusion control and mixing control of the solid product layer. Therefore, it is preliminarily believed that the histidine leaching process was controlled by surface chemical reactions, which is further confirmed by the calculation of the activation energy of the reaction. The apparent activation energy for the leaching reaction was calculated by the Arrhenius equation and the results are shown in Figure 9. It is widely acknowledged that the apparent activation energy (Ea) is less than 12.5 kJ/mol, indicating that the leaching process is diffusion-controlled in the product layer. If 12<Ea<41.8 kJ/mol, the leaching process is mixed-controlled process. When Ea>41.8 kJ/mol, the leaching process is chemical reaction-controlled process[37].

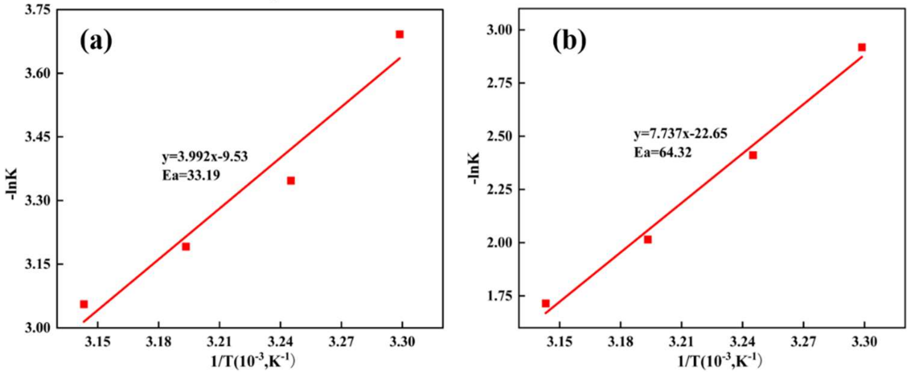

Figure 9. Arrhenius plots for (a) internal diffusion and (b) chemical reaction at different temperatures

Table 3 The activation energy of two control models

Control model	Slope k′	Correlation coefficient(R2)	Ea (kJ/mol)
Chemical reaction control	7.74	0.99	64.32
Internal diffusion control	3.99	0.95	33.19

The results in Fig.9 and Table 3 show that the surface chemical control kinetic model at different temperatures has a good fitting effect, and the correlation coefficient(R_2) was 0.99. The apparent activation energy (Ea) for the cobalt leaching process was 64.32 kJ/mol, which was consistent with the activation energy Ea>41.8 kJ/mol, indicating that the cobalt leaching process mainly conformed to the surface chemical control model and was consistent with the results obtained by fitting the kinetic model (Table 2).

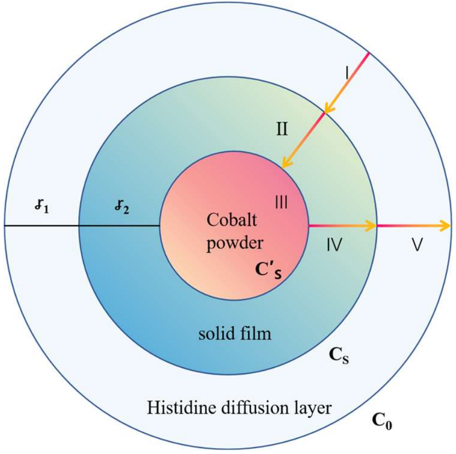

Figure 10. Diagram of the process for leaching cobalt powder with histidine (C_0: leaching agent concentration in water, C_S: leaching agent concentration on the solid surface, C'_S: leaching agent concentration in the reaction zone, δ_1: effective thickness of the leaching agent diffusion layer, δ_2: solid film thickness).

A nucleation model based on the ideal sphere hypothesis is proposed to simulate the leaching process of solid particles. According to the model, the main chemical reaction occurs between the unreacted particle core and the surface of the phase boundary of the reaction product[38]. The leaching process occurs isotropically from the outer surface towards the interior of the spherical particles, preserving the core's spherical configuration, as illustrated in Fig.10. The leaching steps mainly include: I. The leaching agent diffuses towards the surface of the cobalt powder; II. The leaching agent diffuses inward through the solid film; Ⅲ. The leaching agent reacts with cobalt powder; Ⅳ. The product (Co-histidine complex) diffuses out of the reaction site; Ⅴ. The product finally enters the solution through the diffusion layer[39].

5. Conclusions

The recovery of cobalt was efficiently achieved through a selective complexation leaching method utilizing histidine as a green leaching agent. Compared to glycine-based systems, histidine was demonstrated to rapidly form stable soluble complexes with Co^{2+} at lower concentrations across a broader alkaline pH range (6–11). In this study, histidine was innovatively introduced as a sustainable alternative to glycine for cobalt recovery, exhibiting significantly accelerated leaching kinetics (6 h versus 7-672 h for glycine) and enhanced pH adaptability.The leaching process exhibited high selectivity toward cobalt. Under optimized conditions (initial pH 8, 35°C, 0.1 mol/L histidine concentration, 300 rpm stirring speed, histidine/Co molar ratio of 1.5:1, and 12 h duration), extraction efficiencies of 95% Co, 0.7% Fe, 1% Pb, and 1% Cu were attained. Kinetic analysis revealed that cobalt extraction was governed by surface chemical reactions, with an activation energy of 64.32 kJ/mol. The coordination mechanism was confirmed through FT-IR and XPS analyses, which indicated that Co^{2+} in solution predominantly interacted with the -O=C-O- and -N-H functional groups of histidine, leading to the formation of stable chelate ring complexes. This work successfully validated the feasibility of employing histidine as a highly efficient and selective leaching agent for cobalt separation from cobalt-rich alloy slags.

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